DELAYED COKING OF LOW-TEMPERATURE LIGNITE PITCH

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This paper is one of a series on the upgrading and utilization of various low-temperature tar fractions. Previous publications gave details on the preparation of biodegradable detergents from the olefin fraction (1), phthalic and maleic anhydrides from the neutral oil (3), and carbon electrode binders from the thermal cracking of the pitch (2).

Processing of petroleum residuals by delayed coking has been practiced commercially for a number of years (6). Pilot-plant studies have also been carried out on coke oven pitch (7) and a low-temperature tar topped to a temperature of 425° F (4). We believe this is the first effort to extend delayed coking to a low-temperature tar pitch.

MATERIAL, EQUIPMENT, AND PROCESS DESCRIPTION

The tar was produced by the Texas Power & Light Company from a Texas lignite carbonized at 950° F in a fluidized bed. The pitch used in this study was obtained by distilling the crude tar under vacuum to an atmospheric boiling point of 630° F and amounted to 45 percent of the tar. Chemical and physical properties of the pitch are given in Table 1.

The delayed coking apparatus consists of a steel drum (C, see Figure 1) fabricated from a 5-foot length of 8-inch carbon steel pipe. The drum is flanged at the top and bottom ends to make the removal of the coke and cleaning easy. Coke removal is facilitated by use of a tilting drum. The coking drum is heated electrically (15.6 KW max). The pitch feed tank (A) was made from a 15-inch length of 8-inch carbon steel pipe and a cone, with a 1/2-inch coupling at the apex, is welded to the bottom of the 8-inch pipe and the top is open. The pitch tank is electrically heated by a 1.8 KW heater.

The pitch to be coked is ground and liquified in the pitch feed tank by heating to 400° F. The liquid pitch flows to the pitch feed pump (B), a small gear pump driven by an electric motor and hydraulic speed control (J), and is pumped through the pitch line preheater (F) which raises the temperature to about 485° F. The pitch is then fed to the delayed coking drum (C) which is maintained at the desired coking temperature. The pitch remains in the coking drum for several hours while the volatile matters are driven off. The volatiles are fed to an oil and gas condenser (D) and oil is collected in the bottom of the separator (E), and the gas is water scrubbed (H). The gas is then metered (G) and vented. A small tank (K) is tied into the pitch system in such a way that the pitch can be flushed out of the pump with a crude tar distillate fraction. Flushing the pump with crude tar before cooling prevents pitch solidification and simplifies restart.

A photograph of the apparatus is given in Figure 2.

The oil from the separator is vacuum distilled to about 750° F which yields an aromatic-rich distillate and a residue. The distillate can be catalytically oxidized to phthalic and maleic anhydrides while the residue, pitch, can be used as a binder for carbon electrodes, road paving, roofing, or piping material, depending on its specifications, such as softening point, carbon-hydrogen ratio, hydrogen content, and coking value.

RESULTS AND DISCUSSION

This investigation was conducted at temperatures from 800° to 1,200° F and at atmospheric pressure. The coke yield ranged from 25 percent at 800° F to 45 percent at 1,200° F (Figure 3). This increase in yield is due to the higher degradation of the feed pitch at elevated temperatures. The product appeared darker, smoother, and char-like at 800° F, while at 1,200° F the coke had the silver-grey color typical of coke (Figures 4 and 5).

The ash content of the coke, as shown in Figure 6, was the same over the entire range of coking temperatures. The iron content of the coke (Figure 7) also was constant at all temperatures.

The sulfur content of the coke decreased slightly with the increasing temperature, Figure 8, indicating that, at higher temperatures, more of the sulfur was being converted to gas. It has been reported that delayed coke can be used as fuel for generating electric power (5). The relatively low sulfur content of this coke, 0.80 percent, should make it especially attractive as a fuel in view of present air pollution standards.

The coke obtained from this process can also be calcined and used as aggregate in the production of metallurgical electrodes, although the ash is slightly higher than the ash of petroleum coke which is currently used. It is desirable to have an ash content below 0.5 percent in the coke. The coke loses 15 percent by weight when calcined to 2,000° F.

The oil yield is a function of coking temperature and varied from 43 percent of the feed pitch at 800° F to 17 percent at 1,200° F (Figure 3). The specific gravity of the oil was about 0.95 at 800° F and 1.18 at 1,200° F (Figure 9). This oil, when distilled to 720° F, gave a distillate containing from 15 to 25 percent combined acids and bases with the remainder consisting of a neutral oil. The F.I.A. analysis of a typical neutral oil showed 89.2 percent aromatics, 6.9 percent olefins, and 3.9 percent paraffins. The vapor-phase catalytic oxidation of the neutral oil yielded better than 30 percent phthalic and maleic anhydrides. The distillation residue from the oil proved to be a suitable binder for metallurgical electrodes. A detailed evaluation of its use as a binder, as well as the coke as an aggregate, is in progress and will be reported in a future publication.

The gas yield was 17 percent at 800° F and increased to 39 percent at 1,200° F (Figure 3). The effect of coking temperature on the ethylene-to-ethane ratio is shown in Figure 10. This is probably due to dehydrogenation and thermal cracking. In addition, an increase in coking temperature is accompanied by a decrease in the methane-to-hydrogen ratio (shown in Figure 11). This ratio drops from 8:1 at 800° F to about 2:1 at 1,150° F. A typical analysis of gas obtained at 950° F is given in Table II.

CONCLUSIONS

This work has shown that the commercial value of lignite pitch is increased by coking. The coking operation yields three products: oil, gas, and coke. The oil upon distillation is a valuable chemical intermediate. The coke could be used as an aggregate for metallurgical electrodes, other graphite products, and as a low-sulfur fuel. The gas is a possible substitute for natural gas or a source of hydrogen if subjected to a steam reforming process. Ethylene could also be recovered from the gas stream and used as a raw material.

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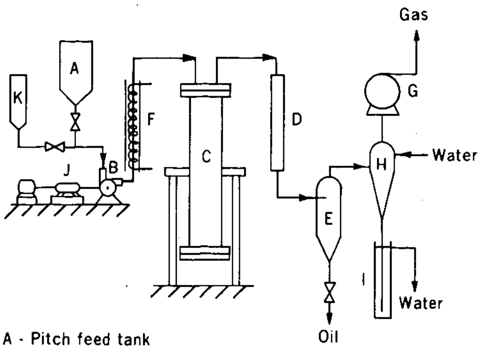
Table I. Properties of Pitch Feed

Ultimate analysis:	As received
Carbon, %	84.72
Hydrogen, %	8.53
Nitrogen, %	0.87
Oxygen, %	4.62
Sulfur, %	0.90
Chlorine, %	0.01
Moisture, %	0.00

Flash point, ° F	510
Softening point (R & B) glycerin, ° C	90
Softening point (cube in glycerin), ° C	105
Penetration at 77° F, 100 grams, 5 seconds	0
Specific gravity, 25° C/25° C	1.128
Ash, %	0.35
Water, %	0.00
Ductility, cm at 77° F	0
Bitumen, soluble in CS_2	78.80
Free carbon	20.85
Distillation:	
To 300° C, %	6.40
Softening point of residue (R & B), ° C	90
Sulfonation index of distillate to 300° C	0
Conradson carbon, %	20.81

Table II. Composition of Gas at a Coking Temperature of 950° F

Component	Volume-percent
CO_2	0.74
CO	4.91
H_2	7.67
CH_4	43.83
C_2H_6	13.97
C_2H_4	9.94
C_3H_8	13.54
C_4^+	5.40



A - Pitch feed tank
B - Pitch feed pump
C - Delayed coking drum
D - Gas and oil cooler
E - Oil separator
F - Pitch line preheater
G - Wet test meter
H - Gas water scrubber
I - Scrubber seal pot
J - Hydraulic speed control
K - Pump flushing oil tank

FIGURE 1. - Flowsheet of Delayed Coking Process.

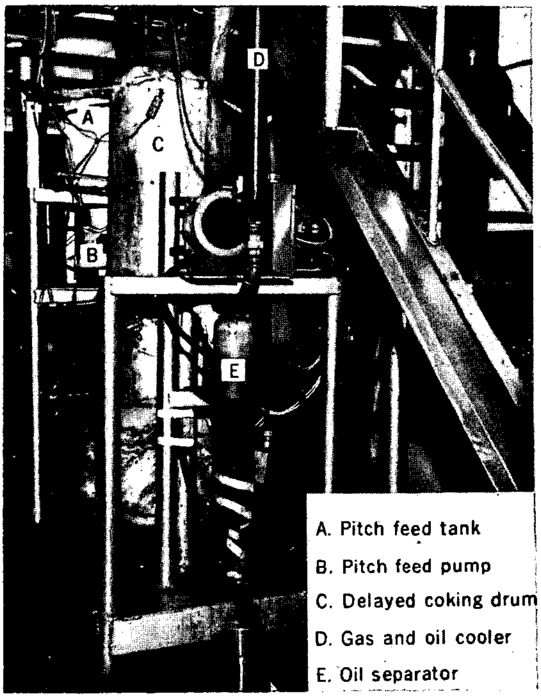


FIGURE 2. - The Delayed Coking Apparatus.

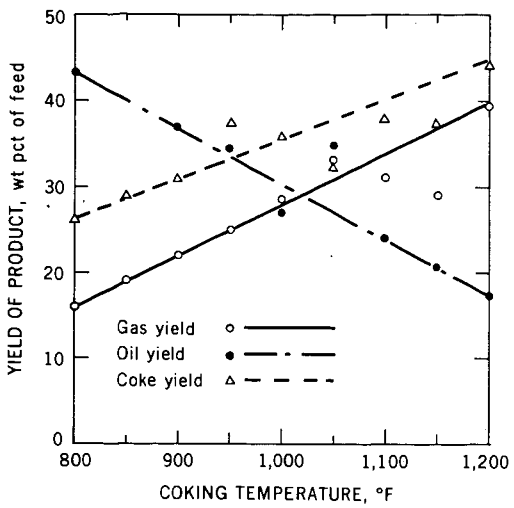


FIGURE 3. - Effect of Temperature on Product Distribution.

FIGURE 4. - Coke at the Top End of the Drum.

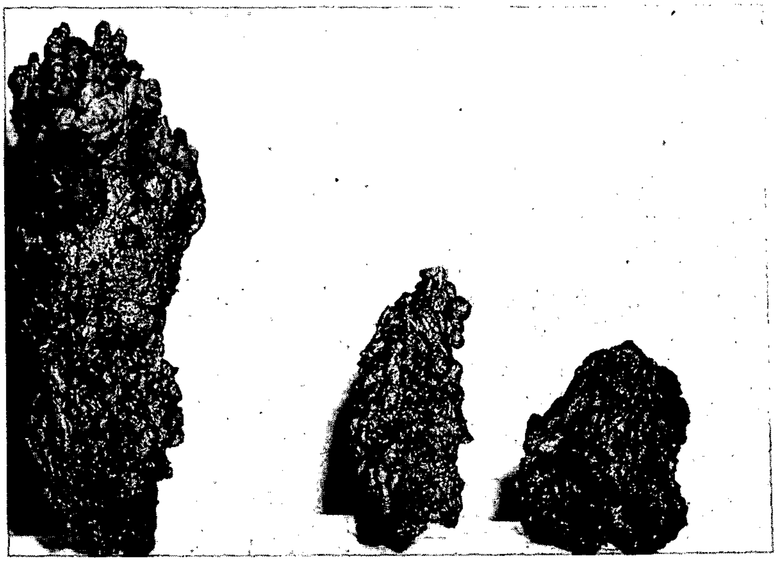


FIGURE 5. - Coke as Taken From Drum.

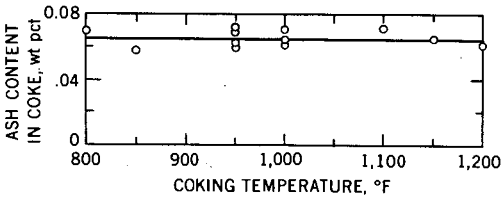


FIGURE 6. - Coking Temperature vs. Ash Content of Coke.

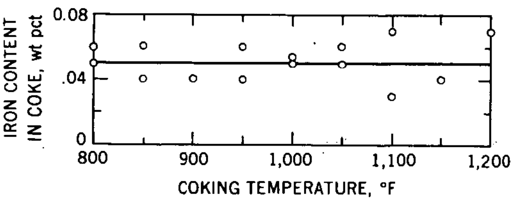


FIGURE 7. - Coking Temperature vs. Iron Content of Coke.

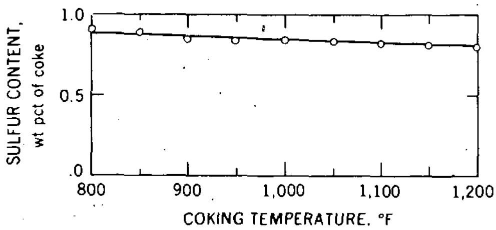


FIGURE 8. - Coking Temperature vs. Sulfur Content of Coke.

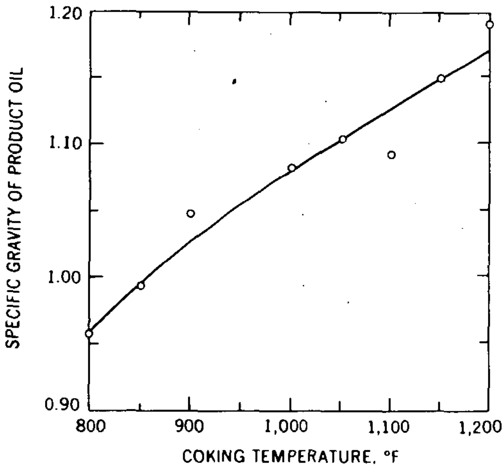


FIGURE 9. - Effect of Temperature on Specific Gravity of Product Oil.

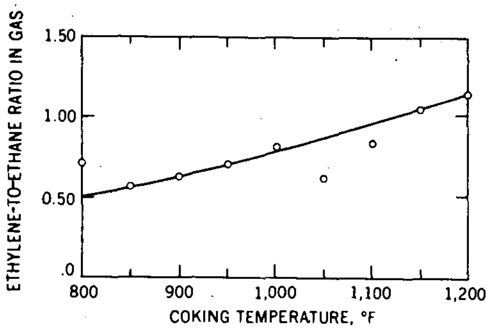


FIGURE 10. - Effect of Temperature on Ethylene-to-Ethane Ratio.

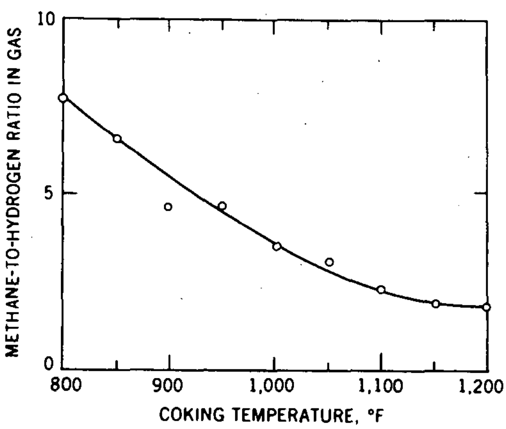


FIGURE 11. - Effect of Temperature on Methane-to-Hydrogen Ratio.